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THERMODYNAMICS OF ANISOTROPIC-GAP AND MULTIBAND CLEAN BCS SUPERCONDUCTORS

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The free energy, non-gradient terms of the Ginzburg-Landau (GL) expansion, and the jump of the specific heat of a multiband anisotropic-gap clean BCS superconductor are derived in the framework of a separable-kernel approximation. Results for a two-band superconductor, *d*-wave superconductor, and some recent models for MgB_2 are worked out as special cases of the general approach. The classical results for the GL coefficients are derived in a simple way, directly from the general expression for the free energy of a BCS superconductor.

Keywords: Ginzburg-Landau theory, specific heat, gap anisotropy, exotic superconductors

1. Introduction

The Landau theory of second-order phase transitions[1] and its realization for superconductors, the Ginzburg-Landau (GL) gauge theory,[2] can be classified as belonging to the most illuminating theoretical achievements in XXth-century physics. The basic concepts advanced in these theories often find applications in interdisciplinary research. The microscopic Bardeen-Cooper-Schrieffer (BCS) theory[3] makes it possible to calculate the parameters of the GL theory. Thus the phenomenology of superconductivity can be reliably derived once the parameters of the microscopic Hamiltonian are specified. Such a scheme ensures that there is no missing link between the microscopic theory and the material properties of the superconductors.

The recent progress in physics of anisotropic-gap superconductors, e.g., cuprates, borocarbides and MgB_2, has attracted considerable attention. However, the analysis of the thermodynamic behavior of these compounds appeared to be erroneous in some cases, and often the results from the classical papers in the field are not taken into account. Thus, the present situation created the necessity that some old theoretical results be delivered in a form suitable for fitting the experimental data.

The purpose of the present paper is to provide a simple methodological derivation of the non-gradient terms of the GL expansion. These are then used to set up

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appropriate for numerical implementation expressions which employ the electron band dispersion and momentum dependence of the gap function at the Fermi surface. We have paid particular attention to reflect the relation of our results to those obtained in the pioneering papers in this field. Employing the Bogoliubov-Valatin method[4,5] and the standard expression for the free energy in the BCS model we present a simple derivation of the results by Pokrovskiĭ and Ryvkin[6] and Gor'kov and Melik-Barkhudarov.[7] We have particularly focused on the jump of the specific heat ΔC at the critical temperature T_c which is expressed through the coefficients of the GL expansion. Finally, the general formulae are applied to derive ΔC in different models used to describe the superconducting cuprates, borocarbides, and MgB_2.

2. Microscopic formalism

Our starting point is the *total reduced* Hamiltonian[8,9,10] for a multiband superconductor with singlet pairing

$$\begin{aligned}\hat{H}' &= \hat{H}_0 - \mu\hat{N} + \hat{H}_{\rm int} \equiv \hat{H}'_0 + \hat{H}_{\rm int} \\ &= \sum_{b,\mathbf{p},\alpha} \xi_{b,\mathbf{p}}\, \hat{c}^{\dagger}_{b,\mathbf{p}\alpha}\hat{c}_{b,\mathbf{p}\alpha} + \frac{1}{\mathcal{N}}\sum_{b,\mathbf{p}}\sum_{b',\mathbf{p}'} V_{b,\mathbf{p};b',\mathbf{p}'}\, \hat{c}^{\dagger}_{b,\mathbf{p}\uparrow}\hat{c}^{\dagger}_{b,-\mathbf{p}\downarrow}\hat{c}_{b',-\mathbf{p}'\downarrow}\hat{c}_{b',\mathbf{p}'\uparrow}. \qquad (1)\end{aligned}$$

Here $\xi_{b,\mathbf{p}} \equiv \varepsilon_{b,\mathbf{p}} - \mu$ is the quasi-particle spectrum of the "primed"[†] non-interacting Hamiltonian $\hat{H}'_0$, with b being the band index, and $\hat{c}^{\dagger}_{b,\mathbf{p}\alpha}$, $\hat{c}_{b,\mathbf{p}\alpha}$ are the quasi-particle creation and annihilation operators, respectively, for the bth band, quasimomentum $\mathbf{p}$, and spin projection $\alpha = \uparrow, \downarrow$. The second, four-fermion term in Eq. (1) is determined by the quasiparticle pairing interaction. The form of the corresponding pairing matrix elements $V_{b,\mathbf{p};b',\mathbf{p}'}$ has been one of the vexing problems in the theory of high-T_c superconductivity as the underlying mechanism giving rise to pairing is still unknown.

However, once the interaction is specified, one can apply the standard BCS treatment[3,10] to obtain an equation for the superconducting gap. For the Hamiltonian (1) this leads to the BCS gap equation of the following familiar form

$$\Delta_{b,\mathbf{p}} = \frac{1}{\mathcal{N}}\sum_{b',\mathbf{p}'}(-V_{b,\mathbf{p};b',\mathbf{p}'})\frac{1-2n_{b',\mathbf{p}'}}{2E_{b',\mathbf{p}'}}\Delta_{b',\mathbf{p}'}, \qquad (2)$$

where

$$E_{b,\mathbf{p}} \equiv \sqrt{\xi^2_{b,\mathbf{p}} + |\Delta_{b,\mathbf{p}}|^2}, \qquad n_{b,\mathbf{p}} = [\exp(E_{b,\mathbf{p}}/k_{\rm B}T)+1]^{-1} \qquad (3)$$

are the quasiparticle energies, and the Fermi filling factors, respectively, $k_{\rm B}$ being the Boltzmann constant, and T the temperature. The summation over the band index b' is restricted to the partially filled (metallic) bands, containing the sheets which compose the Fermi surface.

[†]As usual it is convenient to work at fixed chemical potential μ and introduce $\hat{H}'_0 = \hat{H}_0 - \mu\hat{N}$, where $\hat{N}$ is the quasiparticle number operator.

Generally, the BCS gap equation requires numerical treatment, but for the special class of separable kernels V it can be reduced to a transcendental equation. This is the main reason why the gap symmetry of some exotic high-T_c superconductors is addressed on the basis of model separable kernels. For specific pairing mechanisms, however, it can be shown[11] that the interaction kernel *is* of separable form. As a rule simple model estimates result in a sum of such separable potentials. Therefore, as a next step we make the *separability ansatz*[12] for the pairing interaction kernel

$$V_{b,\mathbf{p};b',\mathbf{p}'} = -G\,\chi^*_{b,\mathbf{p}}\,\chi_{b',\mathbf{p}'}, \tag{4}$$

where G is a parameter, characteristic for the pairing interaction process, and the momentum dependence is determined by the (generally complex-valued) anisotropy function $\chi_{b,\mathbf{p}}$. Due to the separable form of the BCS kernel (4) the temperature and momentum dependences of the gap also factorize,

$$\Delta_{b,\mathbf{p}}(T) = \Xi(T)\,\chi_{b,\mathbf{p}}. \tag{5}$$

As emphasized by Gor'kov and Melik-Barkhudarov[7] the factorization of the superconducting gap into temperature (Ξ) and momentum-dependent (χ) multipliers is a general result due to Pokrovskiĭ and Ryvkin,[6] valid for an arbitrary weak-coupling pairing interaction. The gap anisotropy function is given by the eigenfunction of the pairing kernel corresponding to the lowest eigenvalue. The factorable kernel Eq. (4) is just an interpolating Hamiltonian resulting in the same thermodynamic behavior as that determined by the initial kernel. Hence in what follows, without loss of generality, we shall use a separable interaction. Such a type of interaction, however, arises in lattice multiband models if one considers only local (single-site) interactions.

Substituting Eq. (5) into Eq. (2) and passing from summation (for $\mathcal{N}\to\infty$) to integration according to the general rule in the D-dimensional case

$$\frac{1}{\mathcal{N}}\sum_{\mathbf{p}} f(\mathbf{p}) = \int_0^{2\pi}\!\!\cdots\int_0^{2\pi} \frac{d\mathbf{p}}{(2\pi)^D}\, f(\mathbf{p}) \equiv \langle f\rangle_{\mathbf{p}}\,, \tag{6}$$

we obtain a simple equation for the temperature dependence of the gap,

$$G\sum_b \int_0^{2\pi}\!\!\cdots\int_0^{2\pi} \frac{|\chi_{b,\mathbf{p}}|^2}{2E_{b,\mathbf{p}}}\,\tanh\!\left(\frac{E_{b,\mathbf{p}}}{2k_{\mathrm{B}}T}\right)\frac{d\mathbf{p}}{(2\pi)^D} = 1, \tag{7}$$

where the quasiparticle spectrum in expanded form reads

$$E_{b,\mathbf{p}} = \left[(\varepsilon_{b,\mathbf{p}} - E_{\mathrm{F}})^2 + |\Xi(T)|^2\,|\chi_{b,\mathbf{p}}|^2\right]^{1/2}, \tag{8}$$

with $E_\mathrm{F}\equiv\mu$ being the Fermi energy. For the ease of the following discussion we shall consider the simplest case of a single band and suppress the band index. This does not entail any restriction on the generality of the derivation.

3. Thermodynamic properties

In order to implement the GL idea for representing the free energy as a function of the superconducting order parameter, $F(\Xi)$, we shall employ the Bogoliubov-Valatin variational approach.[4,5] Let us recall the main framework of this standard procedure. As a first step one carries out a transformation of the variables, introducing new Fermi operators (for simplicity we will consider real kernels but the appropriate generalization can be easily performed):

$$\begin{pmatrix} \hat{\psi}^{\dagger}_{\mathbf{p}\uparrow} \\ \hat{\psi}_{-\mathbf{p}\downarrow} \end{pmatrix} \equiv \begin{pmatrix} \cos\theta_{\mathbf{p}} & \sin\theta_{\mathbf{p}} \\ -\sin\theta_{\mathbf{p}} & \cos\theta_{\mathbf{p}} \end{pmatrix} \begin{pmatrix} \hat{c}^{\dagger}_{\mathbf{p}\uparrow} \\ \hat{c}_{-\mathbf{p}\downarrow} \end{pmatrix}. \tag{9}$$

Defining the BCS ground state

$$|\mathrm{BCS}\rangle = \prod_{\mathbf{p}} \left(\cos\theta_{\mathbf{p}} + \sin\theta_{\mathbf{p}}\, \hat{c}^{\dagger}_{\mathbf{p}\uparrow}\hat{c}^{\dagger}_{-\mathbf{p}\downarrow}\right)|0\rangle, \tag{10}$$

it is easily verified that $\hat{\psi}_{\mathbf{p}\alpha}|\mathrm{BCS}\rangle = 0 = \hat{c}_{\mathbf{p}\alpha}|0\rangle$, and $\langle \mathrm{BCS}|\,\mathrm{BCS}\rangle = 1 = \langle 0|0\rangle$. The superconducting gap function is then used for a suitable parameterization of the $\theta_{\mathbf{p}}$ angle, $\tan 2\theta_{\mathbf{p}} = \Delta_{\mathbf{p}}/\xi_{\mathbf{p}}$. Denoting $u_{\mathbf{p}} \equiv \cos\theta_{\mathbf{p}}$, $v_{\mathbf{p}} \equiv \sin\theta_{\mathbf{p}}$,

$$u^2_{\mathbf{p}} = \frac{1}{2}\left(1 + \frac{\xi_{\mathbf{p}}}{E_{\mathbf{p}}}\right), \qquad v^2_{\mathbf{p}} = \frac{1}{2}\left(1 - \frac{\xi_{\mathbf{p}}}{E_{\mathbf{p}}}\right), \tag{11}$$

it is straightforward to verify that the condensation amplitude $2u_{\mathbf{p}}v_{\mathbf{p}}$ and coherence factor $u^2_{\mathbf{p}} - v^2_{\mathbf{p}}$ read, respectively,

$$2u_{\mathbf{p}}v_{\mathbf{p}} = \sin 2\theta_{\mathbf{p}} = \frac{\Delta_{\mathbf{p}}}{E_{\mathbf{p}}}, \qquad u^2_{\mathbf{p}} - v^2_{\mathbf{p}} = \cos 2\theta_{\mathbf{p}} = \frac{\xi_{\mathbf{p}}}{E_{\mathbf{p}}}. \tag{12}$$

Within the self-consistent BCS approximation the $\hat{\psi}$-“particles” can be considered as noninteracting, and their thermal-averaged number and entropy are given by the familiar expressions, respectively,

$$n_{\mathbf{p}} \equiv \langle \hat{n}_{\mathbf{p}\alpha}\rangle = \langle \hat{\psi}^{\dagger}_{\mathbf{p}\alpha}\hat{\psi}_{\mathbf{p}\alpha}\rangle = [\exp(E_{\mathbf{p}}/k_{\mathrm{B}}T) + 1]^{-1}, \tag{13}$$

$$S(T) = -2k_{\mathrm{B}} \sum_{\mathbf{p}} \left[n_{\mathbf{p}} \ln n_{\mathbf{p}} + (1 - n_{\mathbf{p}}) \ln(1 - n_{\mathbf{p}})\right]. \tag{14}$$

Similarly, substituting in Eq. (1)

$$\begin{pmatrix} \hat{c}^{\dagger}_{\mathbf{p}\uparrow} \\ \hat{c}_{-\mathbf{p}\downarrow} \end{pmatrix} = \begin{pmatrix} u_{\mathbf{p}} & -v_{\mathbf{p}} \\ v_{\mathbf{p}} & u_{\mathbf{p}} \end{pmatrix} \begin{pmatrix} \hat{\psi}^{\dagger}_{\mathbf{p}\uparrow} \\ \hat{\psi}_{-\mathbf{p}\downarrow} \end{pmatrix} \tag{15}$$

we obtain for the expectation value of the reduced Hamiltonian with respect to the BCS ground state (10)

$$\langle \hat{H}'\rangle = 2\sum_{\mathbf{p}} \xi_{\mathbf{p}} \left[v^2_{\mathbf{p}} + \left(u^2_{\mathbf{p}} - v^2_{\mathbf{p}}\right) n_{\mathbf{p}}\right] - \frac{G}{\mathcal{N}} \left|\sum_{\mathbf{p}} \chi_{\mathbf{p}} u_{\mathbf{p}} v_{\mathbf{p}} (1 - 2n_{\mathbf{p}})\right|^2. \tag{16}$$

The minimization of the free energy

$$F = \langle \hat{H}' \rangle - TS \tag{17}$$

with respect to $\Delta_{\mathbf{p}}$ leads to the gap equation (7). Then the substitution of the so obtained gap in Eq. (17) gives the desired form of the minimal free energy. It should be noted that in order for us to derive the free energy as a function of the order parameter, $F(\Xi)$, we have to use Eq. (5) as *ansatz*, thereby considering the order parameter Ξ as an independent variable for a fixed momentum dependence of the gap function $\Delta_{\mathbf{p}} = \Xi\chi_{\mathbf{p}}$. Thus, the desired function $F(\Xi, T)$ is obtained from Eq. (17) by substituting the expression for the averaged energy, Eq. (16), and that for the entropy, Eq. (14), which can be also rewritten in the form

$$-TS = \sum_{\mathbf{p}} \left[E_{\mathbf{p}} \tanh \frac{E_{\mathbf{p}}}{2k_{\mathrm{B}}T} - 2k_{\mathrm{B}}T \ln \left(2\cosh \frac{E_{\mathbf{p}}}{2k_{\mathrm{B}}T} \right) \right]. \tag{18}$$

The self-consistent BCS approximation gives an analytical dependence on the order parameter $\Delta_{\mathbf{p}} = \Xi\,\chi_{\mathbf{p}}$,

$$\begin{aligned} \frac{F(\Xi,T)}{\mathcal{N}} = {} & 2\left\langle \xi_{\mathbf{p}} \left[\frac{1}{2}\left(1 - \frac{\xi_{\mathbf{p}}}{E_{\mathbf{p}}}\right) + \frac{\xi_{\mathbf{p}}}{E_{\mathbf{p}}} \frac{1}{\exp(E_{\mathbf{p}}/k_{\mathrm{B}}T) + 1} \right] \right\rangle_{\mathbf{p}} \\ & - G \left| \left\langle \frac{|\chi_{\mathbf{p}}|^2}{2E_{\mathbf{p}}} \tanh \frac{E_{\mathbf{p}}}{2k_{\mathrm{B}}T} \right\rangle_{\mathbf{p}} \right|^2 |\Xi|^2 \\ & + 2k_{\mathrm{B}}T \left\langle \frac{E_{\mathbf{p}}}{2k_{\mathrm{B}}T} \tanh \frac{E_{\mathbf{p}}}{2k_{\mathrm{B}}T} - \ln \left(2\cosh \frac{E_{\mathbf{p}}}{2k_{\mathrm{B}}T} \right) \right\rangle_{\mathbf{p}}. \end{aligned} \tag{19}$$

Then the Taylor expansion provides the coefficients in the GL functional per unit cell

$$\frac{F(\Xi,T)}{\mathcal{N}} \approx a(T)\eta + \frac{1}{2} b(T)\eta^2 + O(\eta^3), \qquad \eta \equiv |\Xi|^2, \tag{20}$$

which is often a satisfactory approximation even far from the critical temperature. Let us mention that close to T_{c}

$$a(T) \approx a_0 \frac{T - T_{\mathrm{c}}}{T_{\mathrm{c}}}, \qquad b(T) \approx b \equiv b(T_c) > 0. \tag{21}$$

The order parameter Ξ, being complex in the general case, is proportional to the GL effective wave function, while η is proportional to the superfluid density.

A straightforward way to obtain the a_0 and b coefficients is to compare the variations with respect to η of the expression (17) and the GL expansion (20).

Introducing the notation $\beta = 1/k_{\rm B}T$ the former reads

$$\begin{aligned}\frac{\delta F}{\delta \eta} = &\left\langle \frac{\xi_{\mathbf{p}}^2|\chi_{\mathbf{p}}|^2}{2E_{\mathbf{p}}^3}\left[1-2n_{\mathbf{p}}-2\beta E_{\mathbf{p}}n_{\mathbf{p}}(1-n_{\mathbf{p}})\right]\right\rangle_{\mathbf{p}} + \beta\left\langle n_{\mathbf{p}}(1-n_{\mathbf{p}})|\chi_{\mathbf{p}}|^2\right\rangle_{\mathbf{p}} \\ &- G\left\langle \frac{|\chi_{\mathbf{p}}|^2}{2E_{\mathbf{p}}}(1-2n_{\mathbf{p}})\right\rangle_{\mathbf{p}}\left[\left\langle \frac{|\chi_{\mathbf{p}}|^2}{2E_{\mathbf{p}}}(1-2n_{\mathbf{p}})\right\rangle_{\mathbf{p}}\right. \\ &\left. -2\eta\left\langle \frac{|\chi_{\mathbf{p}}|^4}{4E_{\mathbf{p}}^3}\left[1-2n_{\mathbf{p}}-2\beta\, E_{\mathbf{p}}n_{\mathbf{p}}(1-n_{\mathbf{p}})\right]\right\rangle_{\mathbf{p}}\right]. \end{aligned} \tag{22}$$

Furthermore, introducing the functions

$$\mathcal{A}(\eta,T) = \left\langle \frac{|\chi_{\mathbf{p}}|^2}{2E_{\mathbf{p}}}(1-2n_{\mathbf{p}})\right\rangle_{\mathbf{p}}, \tag{23}$$

$$\mathcal{B}(\eta,T) = \left\langle \frac{|\chi_{\mathbf{p}}|^2}{2E_{\mathbf{p}}^3}\left[(1-2n_{\mathbf{p}})\xi_{\mathbf{p}}^2 + 2\beta\, E_{\mathbf{p}}|\Delta_{\mathbf{p}}|^2\, n_{\mathbf{p}}(1-n_{\mathbf{p}})\right]\right\rangle_{\mathbf{p}}, \tag{24}$$

Eq. (22) can be cast in the compact form

$$\frac{\delta F}{\delta \eta} = \mathcal{B}(\eta,T)(1-G\mathcal{A}(\eta,T)). \tag{25}$$

Notice that the extremum condition of (25), $1-G\mathcal{A}(\eta,T)=0$, gives the gap equation (7). Now varying Eq. (20) with respect to η and comparing with Eq. (25) we find

$$a_0 = -T_{\rm c}\left.\frac{\partial\mathcal{A}(\eta,T)}{\partial T}\right|_{\eta=0,\,T=T_{\rm c}}, \qquad b = -\left.\frac{\partial\mathcal{A}(\eta,T)}{\partial \eta}\right|_{\eta=0,\,T=T_{\rm c}}, \tag{26}$$

where we have used the identity $\mathcal{B}(0,T_{\rm c}) = \mathcal{A}(0,T_{\rm c}) = 1/G$. Thus, Eq. (20) with Eqs. (21), (23), (24), and (26) provide the complete set of equations which determines the GL free energy of an anisotropic-gap superconductor.

We shall proceed now with working out explicit expressions on the basis of the general relations (26). Taking the corresponding derivatives of $\mathcal{A}(\eta,T)$ the a_0 and b coefficients read

$$a_0 = \frac{1}{4k_{\rm B}T_{\rm c}}\left\langle \frac{|\chi_{\mathbf{p}}|^2}{\cosh^2\nu_{\mathbf{p}}}\right\rangle_{\mathbf{p}}, \qquad b = \frac{1}{4(k_{\rm B}T_{\rm c})^3}\left\langle |\chi_{\mathbf{p}}|^4\, Q(\nu_{\mathbf{p}})\right\rangle_{\mathbf{p}}, \tag{27}$$

where $\nu_{\mathbf{p}} = \xi_{\mathbf{p}}/2k_{\rm B}T_{\rm c}$ and (cf. Ref. 13)

$$Q(x) = \frac{1}{x^2}\left(\frac{\tanh x}{x} - \frac{1}{\cosh^2 x}\right) = \frac{\tanh^2 x}{x^2} + \frac{\tanh x - x}{x^3}. \tag{28}$$

In calculating the momentum averages (27) one has to take into account that the integrands in the momentum-space integrals exhibit sharp maxima at the Fermi surface $\varepsilon_{\mathbf{p}} = E_{\rm F}$. Thus, within acceptable accuracy, one can carry out an integration

along the normal to the Fermi surface whereupon $\nu_{\mathbf{p}}$ may take on values in the interval $(-\infty, +\infty)$ while the longitudinal quasimomentum component $p_{\parallel}$ varies negligibly. Taking into account the numerical values of the integrals $\int_{-\infty}^{+\infty}(\cosh x)^{-2}dx = 2$, and

$$\int_{-\infty}^{\infty} Q(x)dx = 8\sum_{n=0}^{\infty}\int_{0}^{\infty}\frac{dx}{[x^2+\frac{\pi^2}{4}(2n+1)^2]^2} = \frac{16}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^3} = \frac{14}{\pi^2}\zeta(3), \tag{29}$$

where $\zeta(m)$ is the Riemann zeta function,‡ we obtain the desired form

$$a_0 = \left\langle |\chi_{\mathbf{p}}|^2 \right\rangle_{\mathrm{F}}, \qquad b = \frac{7\zeta(3)}{8\pi^2(k_{\mathrm{B}}T_{\mathrm{c}})^2}\left\langle |\chi_{\mathbf{p}}|^4 \right\rangle_{\mathrm{F}}. \tag{30}$$

Equation (30) reproduces the results by Pokrovskiĭ and Ryvkin[6] and Gor'kov and Melik-Barkhudarov[7] obtained for the case of a clean superconductor. The detailed consideration of the influence of nonmagnetic impurities on the anisotropic order parameter was given by Pokrovsky and Pokrovsky.[14] Very recently Kogan[15] has analyzed the macroscopic anisotropy in superconductors with anisotropic gap.

For the momentum-space integrals over the Fermi surface which appear in Eq. (30) we use the notation

$$\langle f(\mathbf{p})\rangle_{\mathrm{F}} \equiv \sum_b \int\cdots\int \delta(\varepsilon_{b,\mathbf{p}} - E_{\mathrm{F}}) f(\mathbf{p})\frac{d\mathbf{p}}{(2\pi)^D} = \sum_b \int\cdots\int_{\varepsilon_{b,\mathbf{p}}=E_{\mathrm{F}}} f(\mathbf{p})\frac{dS_{b,\mathbf{p}}}{v_{b,\mathbf{p}}(2\pi)^D}, \tag{31}$$

where $dS_{b,\mathbf{p}}$ is an infinitesimal surface element of the (possibly fragmented) Fermi surface sheet of the bth energy band, and $\mathbf{v}_{b,\mathbf{p}} = \nabla_{\mathbf{p}}\varepsilon_{b,\mathbf{p}}$ is the quasiparticle "velocity" which according to the present convention has dimension of energy. Conversion to the true velocity can be performed by multiplying the (dimensionless) quasimomentum by $\hbar/a$, where a is the lattice constant. For a conventional electron-phonon pairing mechanism the isotropic gap, $\chi_{\mathbf{p}} \equiv 1$, is often a reasonable approximation. Thereby averaging in Eq. (30) results in the density of states (per spin orientation α) at the Fermi level $\rho_{\mathrm{F}} = \langle 1\rangle_{\mathrm{F}}$. In this important case the general formulae are in agreement with the classical result by Gor'kov[16] (in particular, cf. Eq. (11) in Ref. 16).

In thermodynamics of second-order phase transitions the ratio of the GL coefficients a_0 and b determines the jump of the specific heat[1] per unit cell at the critical temperature, so for superconductors

$$\frac{1}{\mathcal{N}}(C_{\mathrm{s}} - C_{\mathrm{n}})|_{T_{\mathrm{c}}} = \frac{\Delta C}{\mathcal{N}} = \frac{1}{T_{\mathrm{c}}}\frac{a_0^2}{b}, \tag{32}$$

‡This result is easily obtained by employing the infinite-series representation $\tanh(x/2) = 4x\sum_{n=0}^{\infty}\left[\pi^2(2n+1)^2 + x^2\right]^{-1}$, and recalling the relation between the Hurwitz and the Riemann zeta functions, respectively, $\zeta(m,\frac{1}{2}) = \sum_{n=0}^{\infty} 1/(n+\frac{1}{2})^m = (2^m-1)\zeta(m)$.

where $C_{\rm s}$ is the specific heat of the superconducting phase, and

$$\left.\frac{C_{\rm n}}{\mathcal{N}}\right|_{T_{\rm c}} = \frac{2}{3}\pi^2 k_{\rm B}^2 \rho_{\rm F}\, T_{\rm c} \tag{33}$$

is the normal-phase specific heat per unit cell at $T_{\rm c}$; the factor 2 takes into account the spin degeneracy of the normal paramagnetic phase. These formulae can be derived directly from the BCS expression for the specific heat[3,17]

$$\frac{C(T)}{\mathcal{N}} = T\frac{d}{dT}\frac{S(T)}{\mathcal{N}} = \frac{2}{k_{\rm B}T^2}\left\langle n_{\mathbf{p}}(1-n_{\mathbf{p}})\left(E_{\mathbf{p}}^2 - \frac{T}{2}\frac{d}{dT}|\Delta_{\mathbf{p}}(T)|^2\right)\right\rangle_{\mathbf{p}}. \tag{34}$$

Substituting Eq. (30) into (32), and taking into account that the order parameter Ξ is not affected by momentum averaging, one finds the general expression for the relative jump of the specific heat of an anisotropic-gap superconductor

$$\left.\frac{\Delta C}{C_{\rm n}}\right|_{T_{\rm c}} = \frac{12}{7\zeta(3)}\frac{1}{\beta_\Delta}, \qquad \frac{1}{\beta_\Delta} = \frac{\left\langle|\Delta_{\mathbf{p}}|^2\right\rangle_{\rm F}^2}{\langle 1\rangle_{\rm F}\left\langle|\Delta_{\mathbf{p}}|^4\right\rangle_{\rm F}} \leqslant 1, \qquad \frac{12}{7\zeta(3)} = 1.42613\ldots, \tag{35}$$

the latter being the universal BCS ratio.[§] Note that β_Δ is similar to the Abrikosov parameter[18] β_A.

4. Applications

4.1. *Jump of the specific heat for layered cuprates*

In models for layered cuprates one often postulates the following functional form of the gap anisotropy

$$\Delta_{\mathbf{p}} \propto \cos(2\phi_{\mathbf{p}}),$$

where $\phi_{\mathbf{p}} = \arctan(p_y/p_x)$. In the case of a parabolic dispersion, $\varepsilon_{\mathbf{p}} \propto p^2$, averaging in Eq. (35) is straightforward and yields

$$1/\beta_\Delta = 2/3.$$

This value should be considered as a lower bound for $1/\beta_\Delta$ as the Fermi velocity is minimal where the superconducting gap is maximal. Consistent with that, for a realistic band dispersion[19] and gap anisotropy[11] the reduction factor may well reach $1/\beta_\Delta = 0.72$.

As pointed out by Abrikosov,[20] if the Fermi level is very close to an extended saddle-point singularity the derivation of the GL equations requires a special consideration.

[§]The numerical value for the specific heat "anomaly" at $T_{\rm c}$ cited originally by Bardeen, Cooper and Schrieffer[3] is slightly different, $\Delta C/C_{\rm n}|_{T_{\rm c}} = 1.52$.

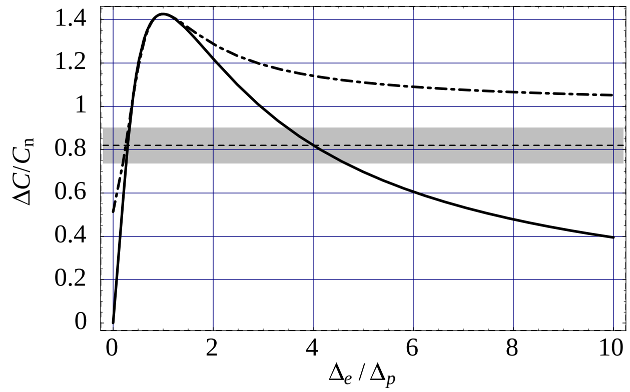

Figure 1: Jump of the specific heat $\Delta C/C_{\rm n}|_{T_{\rm c}}$ versus the "equatorial-to-polar" gap ratio Δ_e/Δ_p. For a given $\Delta C/C_{\rm n}|_{T_{\rm c}}$ value we have oblate $\Delta_e/\Delta_p > 1$ and prolate $\Delta_e/\Delta_p < 1$ solutions. The solid curve[24] represents Eq. (36), and is applicable to the model by Posazhennikova, Dahm and Maki.[21] The dash-dotted line is our analytical solution,[25] Eq. (37), applicable for the model by Haas and Maki.[23] The dashed line is the jump ratio $\Delta C/C_{\rm n}|_{T_{\rm c}} = 0.82 \pm 10\%$ measured by Wang, Plackowski, and Junod,[22] with the shaded area showing the experimental error bar.

4.2. *Jump of the specific heat for* MgB_2

Let us now make some comparison between different models applied to MgB_2. In a very recent e-print Posazhennikova, Dahm and Maki[21] discuss a model for the gap anisotropy in MgB_2, a material which has attracted a lot of attention from condensed-matter physicists in the past two years. A central issue in this work[21] is to propose an analytic model for analyzing thermodynamic behavior. Assuming a spherical Fermi surface, a simple gap anisotropy function is suggested, $\Delta(\mathbf{p}) = \Delta_e/\sqrt{1+Az^2}$, where $z = \cos\theta$, and θ is the polar angle. This model leads to useful results for the temperature dependence of the upper critical field $H_{\rm c2}$ and of the specific heat, which can be fitted to the experimental data, thereby determining the optimal anisotropy parameter A. Note that $A = (\Delta_e/\Delta_p)^2 - 1$, with $\Delta_p = \Delta(z=1)$ and $\Delta_e = \Delta(z=0)$, and the gap ratio is parameterized as $\Delta_e/\Delta_p = \sqrt{1+A} > 0$.

We shall now apply the general results obtained in Sec. 3 to derive a convenient analytical expression giving the possibility for determining Δ_e/Δ_p from the available data for the jump of the specific heat.[22] Following the weak-coupling BCS approach,[21,23] from Eq. (35) we find[24] for $A > 0$, and $-1 < A < 0$, respectively,

$$\left.\frac{\Delta C(A)}{C_{\rm n}}\right|_{T_{\rm c}} = \begin{cases} \dfrac{12}{7\zeta(3)}\dfrac{2(1+w^2)\,(\arctan w)^2}{w^2+w(1+w^2)\arctan w}, & w=\sqrt{A}=\sqrt{\left(\frac{\Delta_e}{\Delta_p}\right)^2-1}, \\[2ex] \dfrac{12}{7\zeta(3)}\dfrac{2(1-y^2)\left(\tanh^{-1}y\right)^2}{y^2+y(1-y^2)\tanh^{-1}y}, & y=iw=\sqrt{-A}=\sqrt{1-\left(\frac{\Delta_e}{\Delta_p}\right)^2}. \end{cases} \tag{36}$$

For a given specific-heat jump, this expression leads to *two* solutions (oblate, $\Delta_e/\Delta_p > 1$, and prolate, $\Delta_e/\Delta_p < 1$). The relevant example is shown in Fig. 1. In Ref. 21 values of $\Delta C(A)/C_\mathrm{n}|_{T_\mathrm{c}}$ consistent with Eq. (36) have been tabulated. The analysis of the experimental data[26,27] for the angular dependence of $H_{\mathrm{c}2}$ unambiguously demonstrates that one has to analyze only the "oblate" case. The experimental value $\Delta C/C_\mathrm{n}|_{T_\mathrm{c}} = 0.82 \pm 10\%$, reported in Ref. 22, gives $A \approx 16$ and $\Delta_e/\Delta_p \approx w \approx 4.0 \pm 10\%$. For this significant anisotropy, the "distribution" of Cooper pairs $\langle|\Delta_\mathbf{p}|^2\rangle \propto 1/[p_z^2 + (p_\mathrm{F}/w)^2]$ has a maximum at $p_z = 0$, and p_F is the Fermi momentum. This general qualitative conclusion is in agreement with the hints from band calculations that the maximal order parameter is concentrated in a nearly two-dimensional electron band, but all bands $\varepsilon_{b,\mathbf{p}}$ contribute to $C_\mathrm{n}/\mathcal{N}$.

In another paper Haas and Maki[23] considered the model gap anisotropy $\Delta \propto 1 + az^2$ for which similar calculation gives[25]

$$\left.\frac{\Delta C}{C_\mathrm{n}}\right|_{T_\mathrm{c}} = \frac{12}{7\zeta(3)} \frac{1 + 4a/3 + 38a^2/45 + 4a^3/15 + a^4/25}{1 + 4a/3 + 6a^2/5 + 4a^3/7 + a^4/9},$$
$$a = \frac{1}{\Delta_e/\Delta_p} - 1, \qquad \Delta_e/\Delta_p = \frac{1}{1+a}. \tag{37}$$

This model, however, cannot explain the significant reduction of $\Delta C/C_\mathrm{n}|_{T_\mathrm{c}}$ observed experimentally, as can be seen in Fig. 1.

4.2.1. $\Delta C/C_\mathrm{n}|_{T_\mathrm{c}}$ *within a two-band model*

For the Moskalenko[8]-two-band model, advocated for the first time for MgB_2 in Ref. 28, Eq. (35) gives (to within a typographical correction) the result by Moskalenko,[8]

$$\left.\frac{\Delta C}{C_\mathrm{n}}\right|_{T_\mathrm{c}} = \frac{12}{7\zeta(3)} \frac{(|\Delta_1|^2\rho_1 + |\Delta_2|^2\rho_2)^2}{(\rho_1+\rho_2)(|\Delta_1|^4\rho_1 + |\Delta_2|^4\rho_2)}$$
$$= 1.426\,\frac{[\delta^2 x + (1-x)]^2}{\delta^4 x + (1-x)} < 1.43, \tag{38}$$

where

$$\delta = \frac{\Delta_1}{\Delta_2}, \qquad x = \frac{\rho_1}{\rho_1+\rho_2},$$

and ρ_1 and ρ_2 are the densities of states for the two bands at the Fermi level. In Fig. 2 we present the specific heat jump as a function of δ for various values of x. Taking for an illustration $x = 0.515$ and $\Delta C/C_\mathrm{n}|_{T_\mathrm{c}} = 0.82$, Eq. (38) gives $\Delta_1/\Delta_2 \approx 4.0$ in agreement with the maximal-to-minimal-gap ratio $\Delta_e/\Delta_p \approx 4.0$ obtained using Eq. (36).

We should stress here that the two-band model also describes a kind of "anisotropy" in the sense that a "*non-constant*" order parameter, having *different constant values* within the different bands comprising the Fermi surface, leads to modified GL parameters and reduces the jump of the specific heat. For a survey on a set

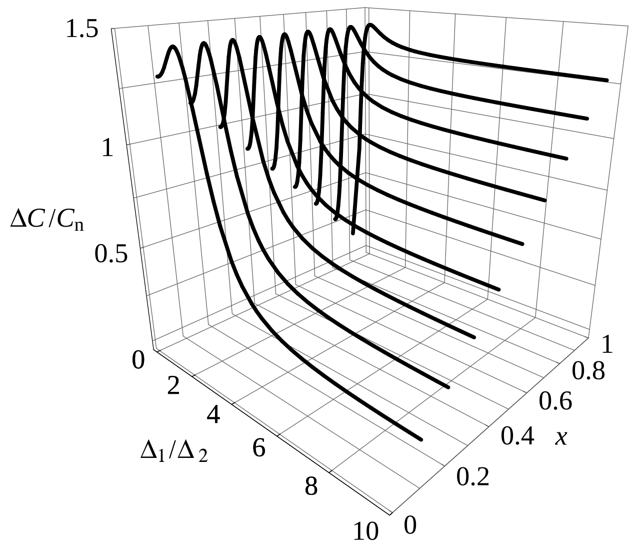

Figure 2: Jump of the specific heat $\Delta C/C_{\rm n}$ at T_c versus the gap ratio Δ_1/Δ_2 for a set of different x values. The latter parameter is the relative contribution of the "first" band to the density of states within the two-band model for MgB_2.

of parameters see Table I in Ref. 29. Certainly, from the jump of the specific heat alone one cannot judge about the validity of any model, so subtleties, e.g., related to strong coupling effects and other anisotropies, can be hidden in the spread of the parameters in the table mentioned.

As we have aimed here on methodological aspects as well, it is beyond the scope of this work to analyze in detail different experimental data and the theoretical fits to them. Nonetheless we shall mention that the Moskalenko-two-band model[8] with isotropic gaps agrees better[29] with the experimental data for MgB_2 compared to other proposed models, but it would be premature to make any final judgment. Thus the synthesis of crystals with really sharp transition may well be rendered necessary.

4.3. *Effect of finite Debye frequency* $\omega_{\rm D}$ *for phonon superconductors*

Up to now we have dealt with energy scales corresponding to very high phonon frequencies or exchange interaction. For phonon superconductors, however, we have to take into account only a narrow "layer" of pairing electrons with energies $|\xi_{\mathbf{p}}| < \hbar\omega_{\rm D}$. In this case $\nu_{\mathbf{p}} \in (-\hbar\omega_{\rm D}/2k_{\rm B}T_{\rm c}, +\hbar\omega_{\rm D}/2k_{\rm B}T_{\rm c})$, and according to Eq. (30) we

have

$$a_0 = \left\langle |\chi_{\mathbf{p}}|^2 \right\rangle_{\mathrm{F}} \tanh \frac{\hbar\omega_{\mathrm{D}}}{2k_{\mathrm{B}}T_{\mathrm{c}}},$$
$$b = \frac{1}{8(k_{\mathrm{B}}T_{\mathrm{c}})^2} \left\langle |\chi_{\mathbf{p}}|^4 \right\rangle_{\mathrm{F}} \int_0^{\hbar\omega_{\mathrm{D}}/2k_{\mathrm{B}}T_{\mathrm{c}}} Q(x)dx. \tag{39}$$

For the relative jump of the specific heat, using Eq. (32) and Eq. (35), we obtain

$$\left.\frac{\Delta C}{C_{\mathrm{n}}}\right|_{T_{\mathrm{c}}} = \frac{12}{\pi^2}\frac{1}{\beta_\Delta}\frac{\tanh^2(\hbar\omega_{\mathrm{D}}/2k_{\mathrm{B}}T_{\mathrm{c}})}{\int_0^{\hbar\omega_{\mathrm{D}}/2k_{\mathrm{B}}T_{\mathrm{c}}} Q(x)dx}. \tag{40}$$

Kishore and Lamba[13] have recently shown that the behavior of $\Delta C/T_{\mathrm{c}}$ calculated within the BCS model with finite ω_{D} is very similar to the results by Marsiglio *et al.*[30] and Carbotte[31] obtained from the Eliashberg theory; see also Ref. 32 and Refs. 33, 34. As regards the recent first-principles linear-response calculation[35] for MgB_2 the agreement between the theory and experiment is comparable to the quality of the fit[29] to experimental data employing the original week-coupling two-band model.[8] Precise analysis, however, has manifested[36] a significant temperature dependence of Δ_1/Δ_2, which we interpret as an evidence for strong coupling effects. Further support can be possibly gained from the direct comparison between the calculated relative jump and the week coupling formula Eq. (38).

5. Summary

Analyzing the Ginzburg-Landau coefficients and the jump of the specific heat at T_{c} we were able to establish that a number of special cases discussed in the recent literature on superconducting cuprates, MgB_2 and borocarbides can be easily derived as a consequence of the classical treatment of thermodynamics of anisotropic superconductors carried out in the dawn of the BCS era. It is somewhat strange that all those early papers are not being used in the current literature and a number of results are rediscovered or treated by a numerical brute force. We have cast, where necessary with the proper correction(s), those classical results into a form to be used for fitting the experimental data. The relative jump of the specific heat is one of the most appropriate quantities which can provide important information for the properties of superconductors. Thus, it would be interesting to see an analogous approach for unconventional superconductors[37] as well.

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